

SOLUTION OF HOMEWORK 4

QUESTION 1: Consider a perfect gas contained in a cylinder and separated by a frictionless adiabatic piston into two sections A and B. All changes in B are isothermal, that is, thermostat surrounds B to keep its temperature constant. There is 2.00mol of the gas in each section. Initially $T_A = T_B = 300\text{K}$ $V_A = V_B = 2.00\text{dm}^3$. Energy is supplied as heat to section A and the piston moves to the right reversibly until the final volume of section B is 1.00dm^3 . Calculate (a) ΔS_A and ΔS_B (b) ΔA_B (c) ΔG_B . If you cannot determine the numerical value indicate if the result is greater or smaller than zero.

First of all, we know that the gas is ideal, therefore the equation of state for the gas is:

$$PV = nRT.$$

(a)

The system in section A is heated up, so its temperature rises. On the other hand the system in section B is held at constant temperature because of the thermostat and because the piston is adiabatic (there is no heat flow from A to B). No energy is dissipated in the movement of the piston (the piston is frictionless). Therefore, the changes in the entropy in section B are due to the usual isothermal compression. We derived the formula to describe such a transformation in class and in quiz 4:

$$\Delta S_B = nR \ln \left(\frac{V_B^{\text{final}}}{V_B^{\text{initial}}} \right) = nR \ln 0.5 = 11.5 \frac{\text{J}}{\text{K}}.$$

We do not have enough information to compute the numerical value of the entropy change in section A. But we can prove that the sign of the entropy change is positive. Indeed, we know that the total volume of the two sections is $2.00\text{dm}^3 + 2.00\text{dm}^3 = 4.00\text{dm}^3$. If at the end the volume of the section B is 1.00dm^3 the final volume of section A is 3.00dm^3 , i.e. $V_A^{\text{final}} = 3/2 V_B^{\text{initial}}$. The final pressures must be the same in section A and in section B to reach mechanical equilibrium. The final pressure for the system in section B is:

$$P^{\text{final}} = \frac{nRT}{V} = 2 \frac{nRT}{V} = 2P^{\text{initial}} = 2P.$$

In this way the final temperature in section A becomes:

$$T_B^{\text{final}} = \frac{P^{\text{final}} V_B^{\text{final}}}{nR} = \frac{2P^{\text{initial}} \frac{3}{2} V^{\text{initial}}}{nR} = 3T^{\text{initial}} = 3T.$$

Therefore, the initial and final states in the pressure-volume plane are represented as in the following figure. How can we find a reversible path to go from the initial to the final state? A possible path is reported in figure 2. The entropy from the first path can be computed knowing that there is no work done by the system (or on the system) if the volume does

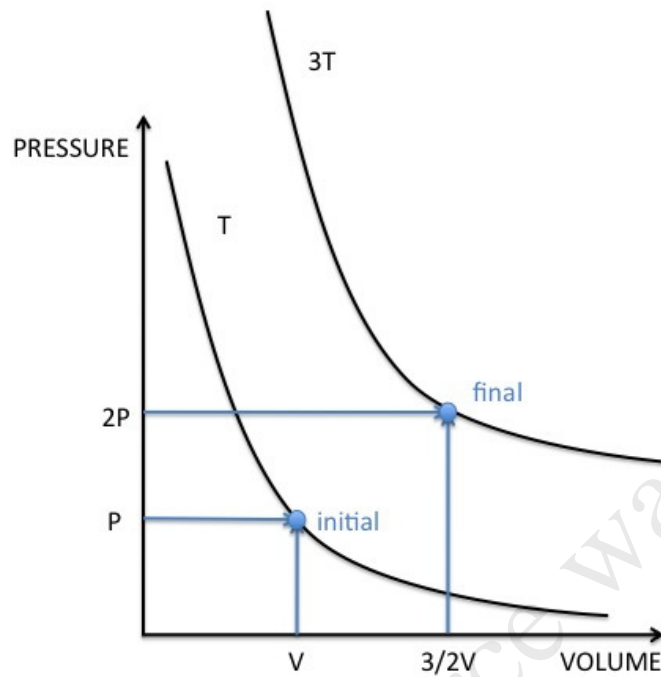


FIGURE 1. The initial and final state are reported in the pressure-volume plane. The black curves are the isotherms corresponding to temperatures T and $3T$.

not change. Therefore, on the first path:

$$dU = C_V dT = dq.$$

And so, knowing that the heat capacity for an ideal gas is a constant, the entropy is

$$\Delta S_{A1} = \int \frac{dq}{T} = C_V \int_T^{3T} \frac{dT}{T} = C_V \ln \frac{3T}{T} = C_V \ln 3.$$

The entropy contribution on the second path is the entropy of an isothermal transformation:

$$\Delta S_{A2} = nR \ln \left(\frac{V_A^{final}}{V_A^{initial}} \right) = nR \ln \frac{3}{2}.$$

The sum of the two gives us:

$$\Delta S_A = C_V \ln 3 + nR \ln \frac{3}{2}.$$

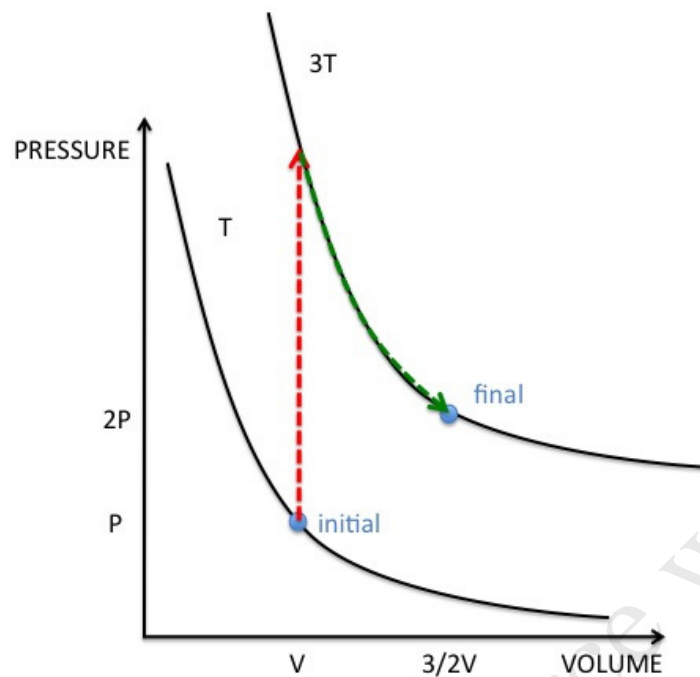


FIGURE 2. Path used to compute the entropy. The first part (red) is constant volume. The second (green) constant temperature.

This is positive. We cannot compute it because we don't know if the gas is monoatomic, diatomic etc.

(b)

The Helmholtz free energy is defined as:

$$A(V, T) = U(V, T) - TS(V, T)$$

For an ideal gas, the internal energy does not depend on the volume of the system, therefore:

$$A(V, T) = U(T) - TS(V, T).$$

The transformation in section B is at constant temperature. Therefore there is no change in the internal energy and we find:

$$\Delta A_B(V, T) = -T\Delta S_B(V, T) = -nRT \ln \left(\frac{V_B^{final}}{V_B^{initial}} \right) = -3450\text{J}.$$

(c)

The Gibbs free energy is defined as:

$$G(P, T) = H(P, T) - TS(P, T).$$

We shown in Quiz 3 that the enthalpy for an ideal gas depends only on the temperature, therefore:

$$G(P, T) = H(T) - TS(P, T).$$

In the isothermal transformation of section B the change in enthalpy is therefore zero. The entropy is a state function, therefore its value depends only on the state it is in. So:

$$\Delta G_B = -T\Delta S_B = -3450\text{J}.$$

QUESTION 2: Find the expression for the change in entropy when two blocks of the same substance and of equal mass, one at temperature T_h and one at temperature T_c are brought into thermal contact and allowed to reach equilibrium. Evaluate the change for two blocks of copper, each of mass 500g with $C_{p,m} = 24.4\text{JK}^{-1}\text{mol}^{-1}$, taking $T_h = 500\text{K}$ and $T_c = 250\text{K}$. Let me refer to the initially cold block as 1 and to the initially hot block as 2 To reach thermal equilibrium, the two blocks will exchange heat. The heat goes from the block at higher temperature to the block at lower temperature. On a reversible path, a small amount of heat exchanged dq_{rev} , causes the following change in entropy of the two blocks:

$$dS = \frac{|dq_{rev}|}{T_c} - \frac{|dq_{rev}|}{T_h}.$$

Here we used the fact that no heat is lost and that the heat goes from the hot block (so the heat flow is $-|dq_{rev}|$) to the cold block (so the change in heat flow is $|dq_{rev}|$). The transformation happens at constant pressure, so we can rewrite:

$$dS = \frac{C_P dT_1}{T_c} + \frac{C_P dT_2}{T_h}.$$

Note here that dT_1 is positive since the temperature of the first copper block will increase, while dT_2 is negative as the temperature of the second will decrease. We can write this expression using the molar heat capacity, defined as the heat capacity per mole:

$$C_P = nC_{P,m}.$$

Therefore,

$$dS = \frac{nC_{P,m}dT}{T_c} + \frac{nC_{P,m}dT}{T_h}.$$

What is the final temperature that the system reaches? Intuitively, we would say that the final temperature is the average of the two temperatures. Indeed, the two blocks are made of the same material and have the same mass. We can actually prove this. If the total heat flowing from one block is equal to the total heat flowing in the second block, than:

$$q_1 = \int_{T_c}^{T_{eq}} n_1 C_{P,m} dT = n_1 C_{P,m} (T_{eq} - T_c) = -q_2 = - \int_{T_h}^{T_{eq}} n_2 C_{P,m} dT = -n_2 C_{P,m} (T_{eq} - T_h).$$

The amount of substance is equal, so $n_1 = n_2 = n$, and the material is the same, so $C_{P,m}$ are equal. Therefore,

$$T_{eq} - T_c = T_h - T_{eq}.$$

So:

$$T_{eq} = \frac{T_c + T_h}{2} = 375\text{K},$$

as expected. Using this, we can compute the change in entropy:

$$\Delta S = \int_{T_c}^{T_{eq}} nC_{P,m} \frac{dT}{T} + \int_{T_{eq}}^{T_h} nC_{P,m} \frac{dT}{T} = nC_{P,m} \left(\ln \frac{T_h + T_c}{2T_c} + \ln \frac{T_h + T_c}{2T_h} \right) = nC_{P,m} \ln \frac{(T_h + T_c)^2}{4T_h T_c}.$$

To prove that this is always positive we must prove that:

$$\frac{(T_h + T_c)^2}{4T_h T_c} \geq 1.$$

This is the same as:

$$T_h^2 + 2T_h T_c + T_c^2 \geq 4T_h T_c.$$

Bringing the right hand side on the left we get:

$$T_h^2 - 2T_h T_c + T_c^2 = (T_h - T_c)^2 \geq 0.$$

Therefore, the entropy increases, as expected. To evaluate the change for copper we need to compute the number of moles of copper that we have. The molar mass of copper is $m = 63.5 \frac{\text{g}}{\text{mol}}$. If the total mass of a block is $M = 500\text{g}$, we have:

$$n = \frac{M}{m} = 7.87\text{mol}.$$

Therefore:

$$\Delta S = 22.6 \frac{\text{J}}{\text{K}}.$$

QUESTION 3: Prove the Maxwell relationships: $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$ and $\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$.

The Helmholtz free energy of a system may be written:

$$dF = \left(\frac{\partial F}{\partial T}\right)_V dT + \left(\frac{\partial F}{\partial V}\right)_T dV = -SdT - pdV.$$

For a function of multiple variables we know that the order of the derivative does not matter, and so:

$$\left[\frac{\partial}{\partial V} \left(\frac{\partial F}{\partial T} \right)_V \right]_T = \left[\frac{\partial}{\partial T} \left(\frac{\partial F}{\partial V} \right)_T \right]_V.$$

Therefore,

$$\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial p}{\partial T} \right)_V$$

In the same way, for the enthalpy we have:

$$dH = \left(\frac{\partial H}{\partial p} \right)_S dp + \left(\frac{\partial H}{\partial S} \right)_p dS = Vdp + TdS.$$

Since, also in this case the order of the second derivatives do not count, we get;

$$\left[\frac{\partial}{\partial S} \left(\frac{\partial H}{\partial p} \right)_S \right]_p = \left[\frac{\partial}{\partial p} \left(\frac{\partial H}{\partial S} \right)_p \right]_S.$$

Therefore:

$$\left(\frac{\partial V}{\partial S} \right)_p = \left(\frac{\partial T}{\partial p} \right)_S$$

BONUS: Given the formula $dU = TdS - pdV$ show that $dS = C_V \frac{dT}{T} + R \frac{dV}{V}$ for one mole of ideal gas. Find the change in entropy for one mole of gas using the change $T_1 V_1 \rightarrow T_2 V_2$.

The expression for the energy can be rewritten as follows:

$$dS = \frac{dU}{T} + \frac{p}{T} dV.$$

For an ideal gas, the internal energy depends only on the temperature, so:

$$dU = C_V dT.$$

Using this and the equation of state

$$p = \frac{nRT}{V}$$

we get:

$$dS = C_V \frac{dT}{T} + nR \frac{dV}{V}.$$

We can think at the path

$$T_1 V_1 \rightarrow T_2 V_2$$

as a two steps reversible process in which the first step is isothermal and the second at constant volume:

$$T_1 V_1 \rightarrow T_1 V_2 \rightarrow T_2 V_2$$

For the first step we have constant T , so $dT = 0$, then:

$$\Delta S_1 = \int_{V_1}^{V_2} nR \frac{dV}{V} = nR \ln \frac{V_2}{V_1}.$$

For the second step we have constant volume, so $dV = 0$, then:

$$\Delta S_2 = \int_{T_1}^{T_2} C_V \frac{dT}{T} = C_V \ln \frac{T_2}{T_1}.$$

Therefore, we get:

$$\Delta S = nR \ln \frac{V_2}{V_1} + C_V \ln \frac{T_2}{T_1}$$